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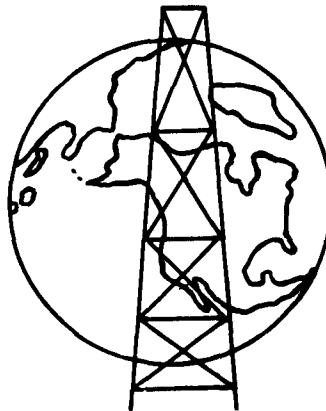
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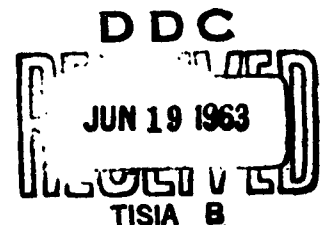
**THE INVESTIGATION OF SOME TECHNIQUES FOR
MEASUREMENT OF HUMIDITY AT HIGH ALTITUDES**

by ROBERT J. CHARLSON and K. J. K. BUETTNER

Prepared for
GEOPHYSICS RESEARCH DIRECTORATE
Air Force Cambridge Laboratories
Office of Aerospace Research
United States Air Force
Bedford, Massachusetts



MARCH 1963



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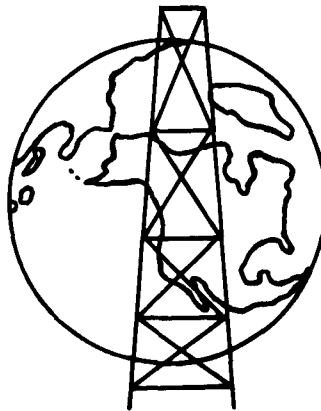
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Abstract

Two approaches to the problem of measuring humidity at high altitudes are described. The first consists of the adaptation of the principle of gas chromatography to the separation of minute amounts of water from air. The laboratory experiments and apparatus are described. A possible design for an automatic chromatographic hygrometer is presented. The second approach consists of the use of the chromatographic packing as the dielectric of a small capacitor. The results of experiments with this new technique are presented. This device is unique inasmuch as its response can be described by an acceptable theory. The results of a literature survey are summarized.

LIST OF PERSONNEL

K. J. K. Buettner
Robert J. Charlson
Gary A. Maykut

Papers Presented

A paper on the methods of humidity measurement herein outlined will be delivered by R. J. Charlson at the International Symposium on Humidity and Moisture, in Washington, D.C., May 20-23, 1963.

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utilizing chromatograph packing

I. INTRODUCTION

The basic purpose of the initial phase of the contract was to conduct theoretical and experimental studies of a gas chromatographic device suitable for measuring the water content of the atmosphere. We were primarily interested in finding the sensitivity and accuracy to measure the minute quantities of water in the stratosphere and mesosphere. Any instrument or design for this purpose has to be compatible with the weight, size and power limitations of the smallest possible meteorological carriers. Other investigations were also included in this initial and exploratory phase. The possibility of using chromatographic techniques for the measurement of other atmospheric constituents, (e.g., ozone, HDO, HTO, CO₂, and C¹⁴O₂) were to be explored.

The main application of the desired instrument is the measurement of stratospheric humidities. Recent data show that anomalously high humidities exist above the tropopause (1,2,3). This increase of mixing ratio with altitude can be attributed to any one or a combination of the following:

1. The production of water by a chemical reaction of the proton-rich solar wind with oxygen in the atmosphere and a corresponding downward flux. (4)
2. The ablation of meteorites and comets near the atmosphere due to the probable large amounts of water in such bodies (re., personal discussion, Prof. E. Anders of Chicago). Once again, a downward flux results.
3. Thin stable lamina (Danielsen layers), known to transport warm air and radioactive dust. (5)

4. Ice clouds in the region of the tropical tropopause, perhaps too thin to be visible, carried away by the high troposphere divergence of the tropics.

5. Supersaturated air transported via the same mechanism as (4). This would require transport times shorter than times required for crystal growth.

The purpose of this report is to summarize the work accomplished and to relate this work to the above problems and to future work. In particular, the progress on the use of a gas chromatograph and the design of a new hygrometer utilizing a chromatographic packing will be described.

II. BASIC CHROMATOGRAPH STUDIES

Early in the research program, it was necessary to decide whether to build a specialized chromatograph or to purchase a commercially available instrument and adapt the latter to our measurements. Because of the availability of an integrated instrument with superior sensitivity and because of the probability of saving several months of design and fabrication time, a commercial instrument was chosen. Vendors were contacted, and the Beckman Instrument Corporation's Model GC-2A was purchased. Some of the features of this instrument are particularly well suited to this research and should be mentioned. The temperature controlled column compartment allows the use of many different sizes and types of columns as well as any temperature between ambient and 240°C. The detector is an extremely sensitive thermal conductivity cell. This hot-wire Wheatstone bridge is the most sensitive available detector short of ionization or flame units. The gas sampling valve allows a variety of sample volumes to be injected in an

efficient fashion onto the column. A dual column valve, available as an accessory, can be used either to operate two columns simultaneously or to bypass the detector when large unwanted peaks could saturate or harm the hot wire elements. This instrumental ensemble was ideally suited to our needs.

With this integrated unit in the laboratory, it was then necessary to fabricate columns suitable for the efficient separation of water vapor from air. The problem at this point included the size of the column as well as the packing material and the liquid phase. Ideally, the column should be short for a minimum elution time and should be fabricated from a chemically inert material. Mr. Theron Johns of Beckman Instruments suggested a 7.5 cm by approximately 0.5 cm diameter column packed with an inert fluorocarbon solid phase. For the liquid phase, it was necessary to resort to a high-boiling polar compound, a polyethylene glycol (Union Carbide Chemicals, Carbowax 400). A fluorocarbon that is prepared especially for chromatographic work is commercially available (Fluoropak 80). This material has a large surface area to mass ratio ($0.64 \text{ m}^2/\text{g}$) so that it is possible to use up to 25% by weight liquid phase without bleeding or flowing. This unique characteristic made possible the experiments described in section V. With this column, it has been possible to detect 50 ppm water vapor in a 1 cc sample of air at 25°C and 1 atmosphere pressure. Figure 1 shows a typical chromatogram for a water analysis.

Larger sample volumes can be used to extend the sensitivity perhaps as much as one order of magnitude. Ten cc sample loops for the gas sampling valve are currently being tested.

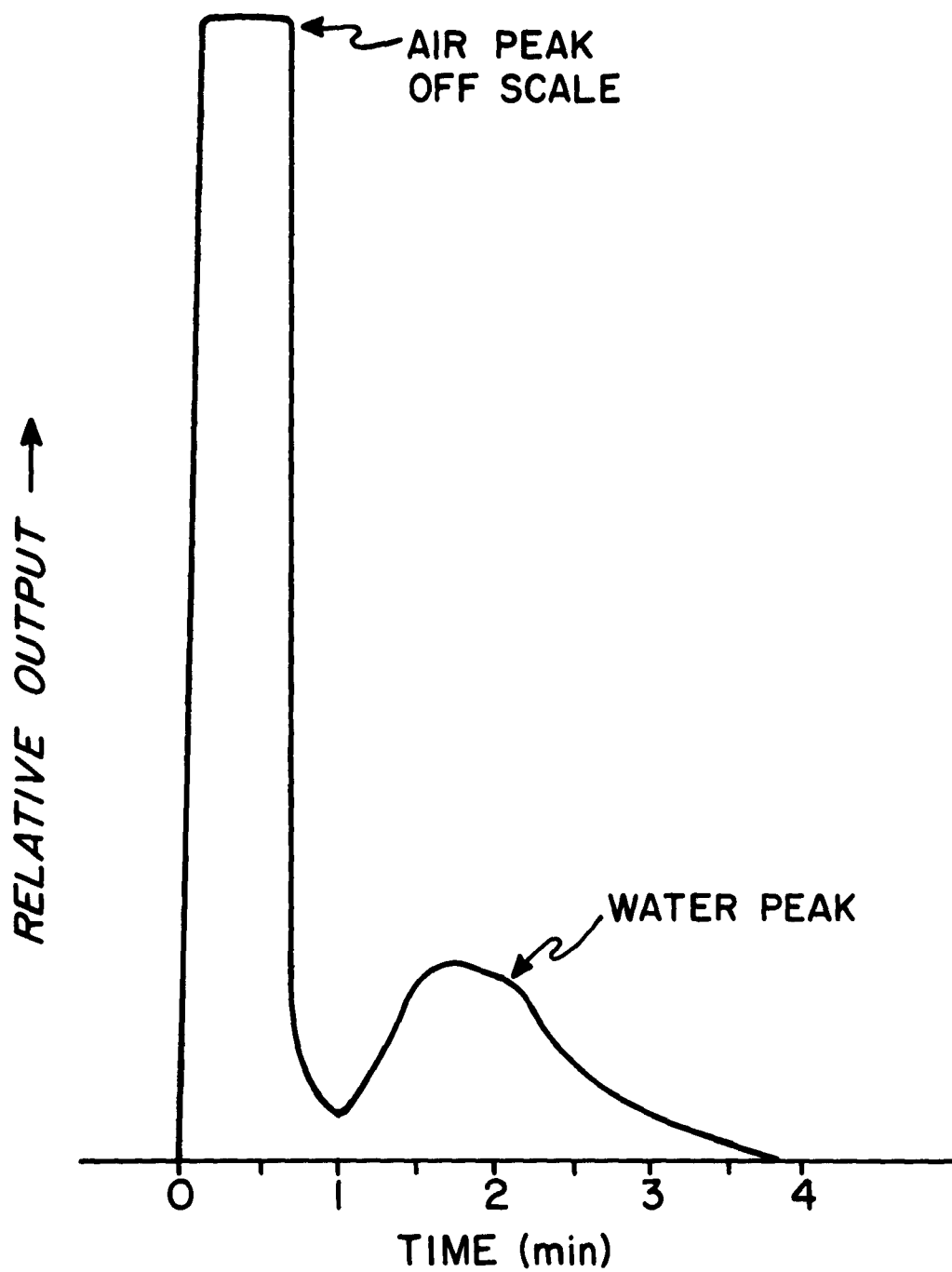


Figure 1

Typical chromatogram; air-water separation.

Results obtained to date with these new sample volumes indicate that a longer column and elution time are necessary and that overloading of the packing may occur.

Because the hot-wire detector must not be exposed to an oxidizing environment when operated at high sensitivity, it was necessary to install a bypass valve so that the air peak would not be detected. Figure 2 illustrates this feature. It would be possible to install another less sensitive hot wire on the exhaust side of the bypass valve to record the amount of air in the sample. Thus, the chromatograph could be utilized as a pressure instrument as well as a hygrometer.

On the basis of the experimental work to date, we have arrived at a design for an automatic chromatographic hygrometer. Because of the several different operations that must be performed in one cycle, the heart of the instrument is a multi-port valve. Figure 3 shows schematically the flow diagram for this instrument as well as the valving sequence.

Several problems can be anticipated during operation of such an instrument. First, the valving scheme must be designed with an absolute minimum of dead volume to insure proper operation of the chromatograph. Second, the effects of large sample volumes at low pressures must be investigated. It is possible that pressure or density variations caused by the compression of the sample to the pressure of the carrier gas might upset the balance of the detector for a period of time greater than the elution time. This effect could probably be removed by proper design of the bypass system.

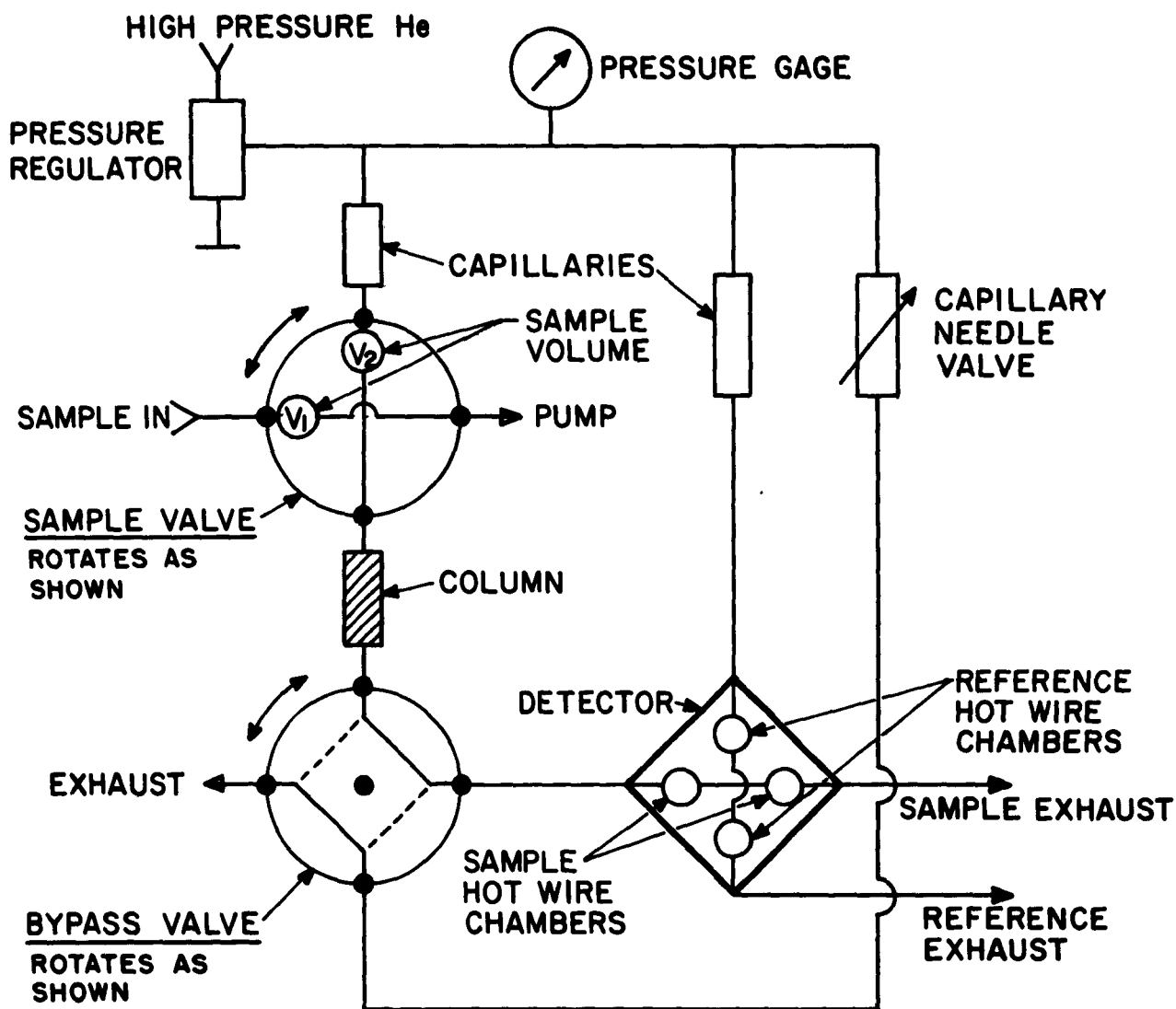


Figure 2

Bypass valve flow scheme as installed in Beckman GC2-A gas chromatograph.

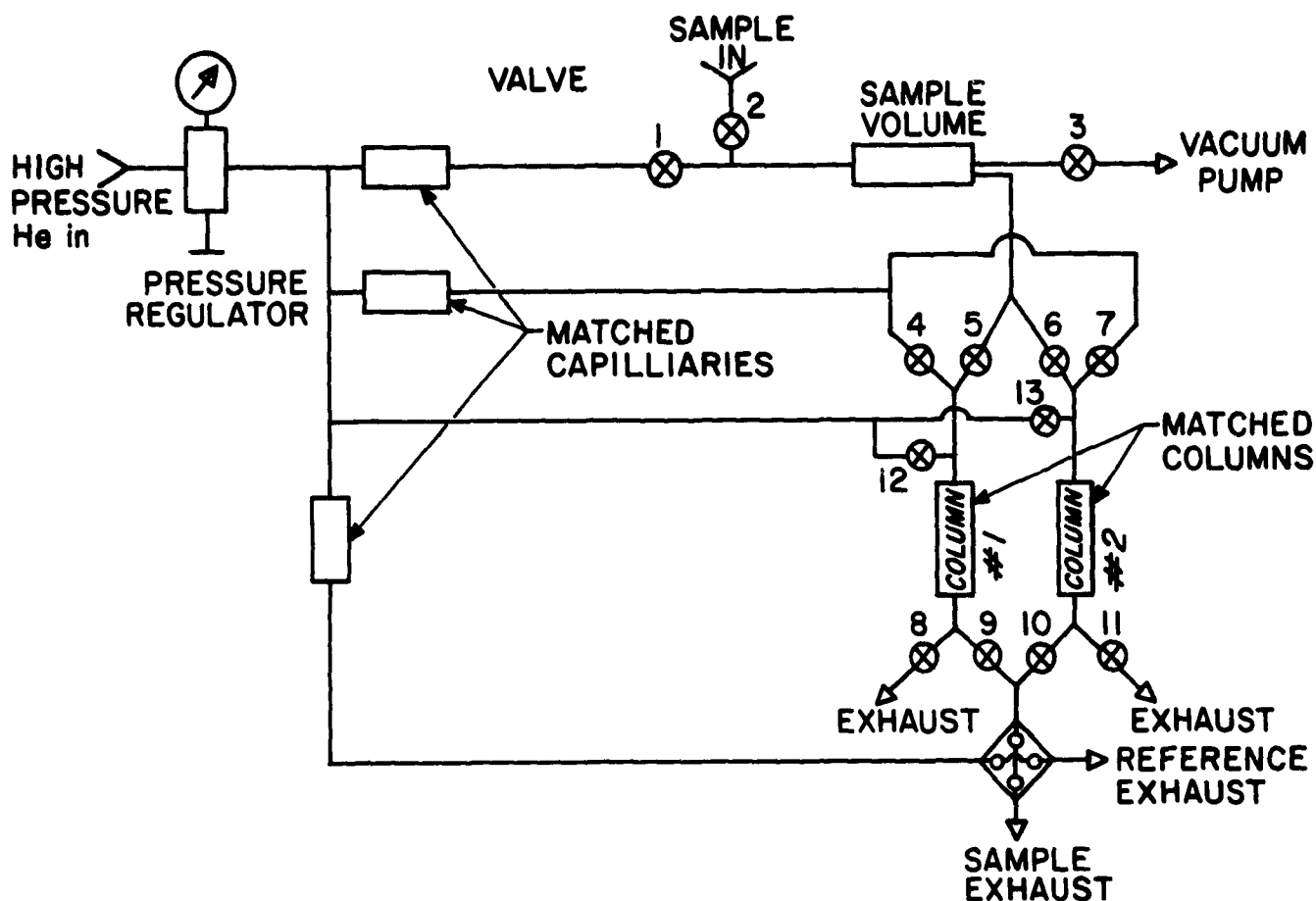


Figure 3

Flow Scheme for Automatic Chromatograph operation.

Valve #	Take in Sample 1 Elute Column 2 Flush Column 1	Load Column 1 Elute & Record Column 2	Take in Sample 2 Elute Column 1 Flush Column 2	Load Column 2 Elute & Load Column 1
1	Closed	Open	Closed	Open
2	O	C	O	C
3	O	C	O	C
4	C	C	O	O
5	C	O	C	C
6	C	C	C	O
7	O	O	C	C
8	O	O	C	C
9	C	C	O	O
10	O	O	C	C
11	C	C	O	O
12	O	C	C	C
13	C	C	O	C

III. CALIBRATION SYSTEM

In order to study stratospheric humidity measurements, it is necessary to have both a source of low relative humidity and some means of measuring it. For this purpose, we have fabricated a flow system that will provide mixing ratios between 10^{-6} and 10^{-3} gH₂O/g(air). This device depends on the mixing of two streams of air; one has been dessicated to a high degree with a Molecular Sieve, the other has been saturated with water vapor over an ice-water mixture. Figure 4 shows schematically the low humidity source. The flow system is sampled by a vacuum pump through a low pressure chamber to simulate the low pressure conditions of the stratosphere. This flow device is ideal for the chromatograph and for other sensors under development in this program. Thus, our simulator is valid for measurements in which a sample flow is obtained (i.e., via pitot pressure aboard an aircraft) in contrast to the more common static devices.

In order to measure the humidity produced by the above source, a Beckman Instruments IR-8 infrared spectrophotometer with a ten meter to ten centimeter variable path gas cell has been ordered. Because of the narrow band pass available and because of the variable path, it will be possible to use the Beer Law for adsorption. On wider band pass instruments it is necessary to resort to more complicated optical absorption laws. This instrument will be installed as part of the calibration flow system so that accurate humidity values will be taken continuously during the calibration of chromatographic or adsorption hygrometers.

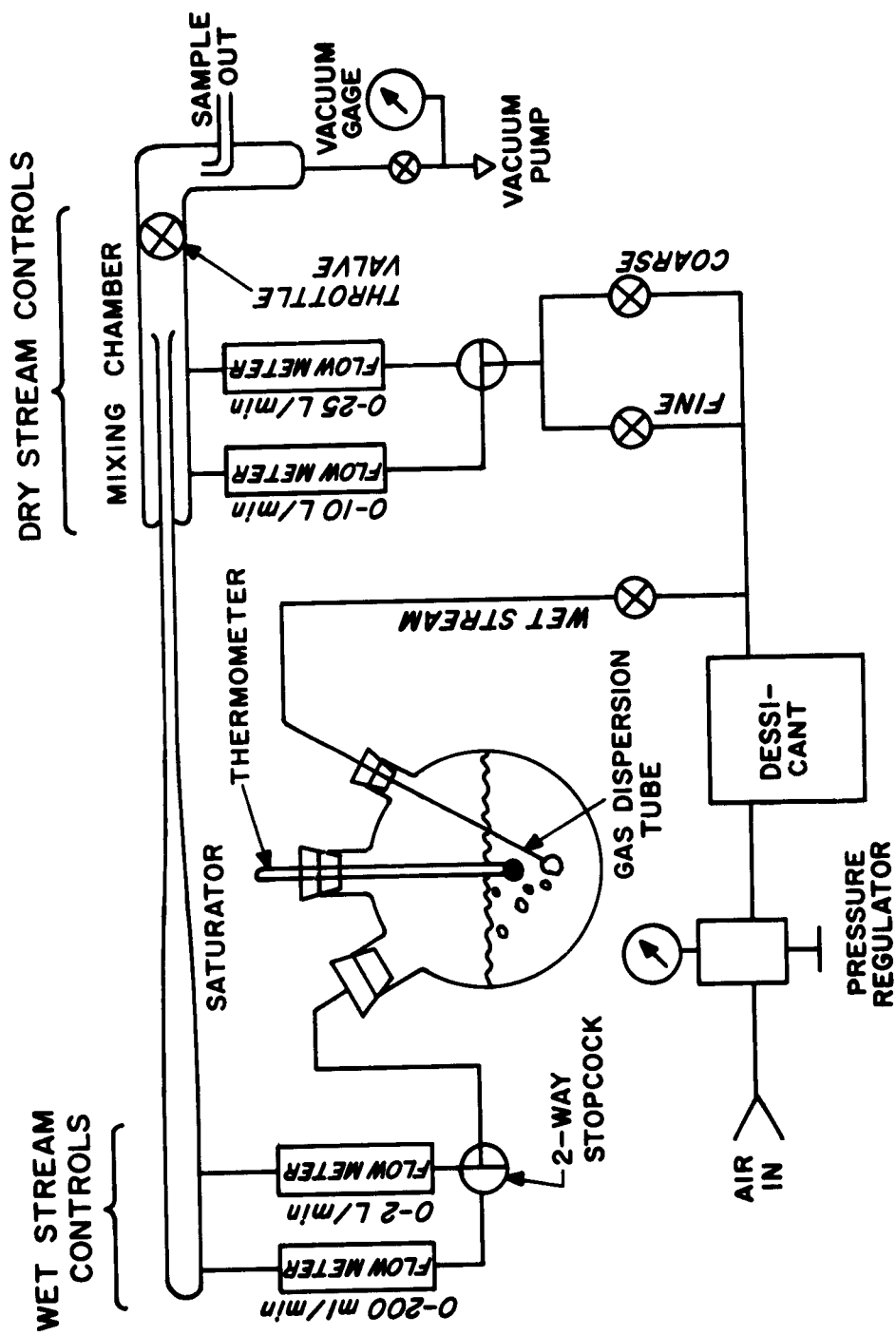


Figure 4
Calibration Apparatus.

IV. ISOTOPE SEPARATIONS VIA THE GAS CHROMATOGRAPH

Several experiments were performed in an attempt to separate HDO and H₂O chromatographically. The techniques used were suggested by members of chemistry Professor Rabinovitch's staff. This group has been able to separate such compounds as CD₃CN and CH₃CN by the use of a Golay column coated with an appropriate liquid phase. These columns consist of a long (30-100 meter) tube on the order of 1-2 mm inside diameter. No packing is used and the liquid phase is coated directly on the walls of the tubing.

Three different columns were built; nylon, polyethylene, and stainless steel were the materials. The first two could not be coated with a suitable liquid phase. The stainless column, however, performed properly and provided information about the desired separation. With a length of 30 meters, it has been possible to obtain as high as 1600 theoretical plates with an elution time of 1.5 hours. (The number of theoretical plates is a figure of merit for a gas-chromatographic separation.) However, even though this number should allow separation of HDO and H₂O, only one peak was observed. Professor Mosher of the Department of Chemistry of Stanford University suggested that the deuteron on the heavy water would exchange with the proton of the hydroxy groups in the liquid phase. Professor Fairhall of the Chemistry Department of this University agreed and added that the rate of exchange would be too high to allow this separation. The reason lies in the high mobility of the proton or deuteron in the water molecule or in the hydroxy groups on an organic molecule. Thus, the utilization of the gas chromatograph for studies of aqueous isotopes seems remote.

It would be possible to perform this separation if the water were converted to H₂ and HD via any of several chemical processes. The hydrogen

isotopes could then be separated by existing techniques. Another possibility would be to incorporate the hydrogen isotopes into an organic molecule (i.e., CH_3D or CDCH) and once again use ordinary chromatographic techniques to attain separation. However, these processes are not simple to achieve in a flow system and do not seem very practical in comparison to other methods such as the mass spectrometer.

V. CAPACITIVE HYGROMETER UTILIZING CHROMATOGRAPH PACKING

As part of an experiment to determine optimum packing properties, a device was assembled for measuring the changes in dielectric constant of the coated Fluoropak granules as a function of the partial pressure of water vapor. Parallel with this experiment, a theoretical approach was made. Both endeavors were successful in showing that the dependence of bulk dielectric constant on humidity is indeed a useful method of measuring low humidities. Because of the utility of this technique, patent proceedings were initiated and are still underway.

If the equilibrium between the thin layer of hygroscopic liquid and water vapor in the ambient air can be considered ideal, it is possible to apply Raoult's Law:

$$(1) \quad \frac{P_w}{P_t} = \frac{N_w}{N_w + N_s} = R$$

P_w = partial pressure of water vapor in the gas flow.

P_t = vapor pressure over pure H_2O at instrument temperature.

N_w = # of moles of H_2O adsorbed in the thin liquid layer at temperature T.

N_s = # of moles of liquid coating.

R = Relative humidity.

Now, the dielectric constant change due to addition of water to the liquid phase can be given by:

$$(2) \quad \Delta C = KN_w$$

ΔC = change in capacitance from zero humidity to some humidity.

K = proportionality constant - experimentally derived but theoretically obtainable.

or, finally:

$$(3) \quad \frac{P_w}{P_T} = \frac{A\Delta C}{A\Delta C + 1}$$

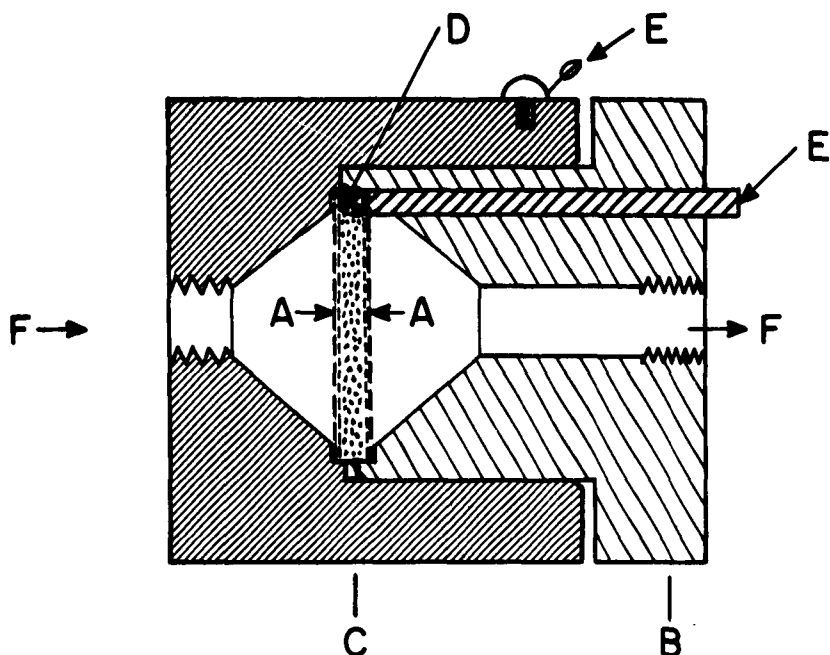
where A is a combined experimentally derived constant.

At low humidities this reduces to:

$$(4) \quad \frac{P_w}{P_T} = R = A\Delta C$$

Physically, this hygrometer is in the form of a pair of parallel porous conductors with the heterogeneous mixture of fluorocarbon granules and liquid contained between. The dimensions are somewhat arbitrary, but typically the conductors are a pair of stainless steel gauze discs of 3 cm diameter spaced about 0.5 mm apart. The dead capacitance is of the order of 50 pF and the sensitivity coefficient, A , is of the order of 0.1 pF^{-1} . Figure 5 is a cross section of the hygrometer.

Experimentally, it has been shown that the capacitive device behaves according to this simple theory within the accuracy of our present readout instrument (a Tektronix type 130LC meter). With this relatively crude electronic device, it has been possible to measure partial pressures of water vapor of 1 mb with about 10% accuracy. The detection limit is presently on the order of 0.1 mb, which corresponds to a frost point of -40°C . Calculations show that we should be able to extend this detection



- A - Capacitor plates on each side of packing
- B - Teflon clamp-plug
- C - Stainless steel body
- D - Packing material
- E - Electrical contacts
- F - Air flow

DETAIL A, D

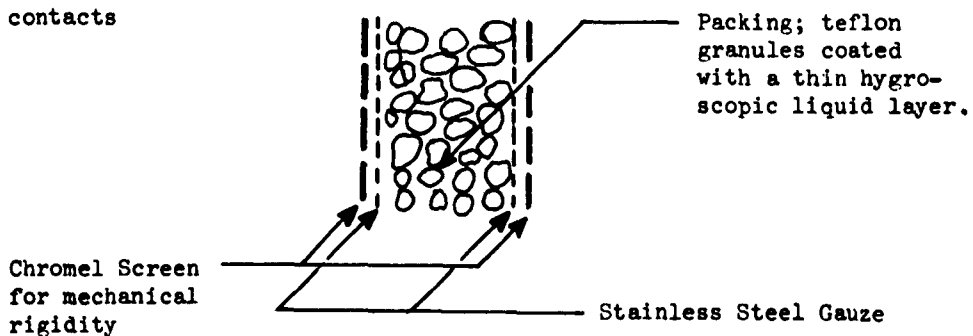


Figure 5

Cross section, thin liquid layer Hygrometer utilizing chromatograph packing.

limit to 10^{-3} or 10^{-4} mb, thus making stratospheric humidity measurements possible. These improvements will consist mainly in electronic revisions and temperature control of the detector.

In operation, this device could be used in three different ways:

1. In thermal equilibrium with the surroundings, the device provides exact relative humidity data. A small detector could possibly be attached to the intake of the present Regener photochemical ozone sonde. This installation would provide relative humidity data on the intake portion of the cycle, and, since the airflow passes over a P_2O_5 dessicant, a zero calibration on exhaust.
2. If the device were enclosed in a temperature controlled chamber and if the air flow were passed through a heat exchanger at the same temperature, then P_T would be fixed (see equations 3 and 4) so that vapor pressure would be measured.
3. If the capacitor were part of a null circuit, it would be possible to use the out-of-balance signal to control the temperature of both the instrument and the air flow so that a vapor pressure balance could be maintained. This technique would alleviate the need for accurate capacitance measurements; the temperature of the device being a sufficient measurement for the determination of humidity.

VI. LITERATURE SURVEY

A literature survey was inaugurated during the first month of the contract. The topics of interest were limited to subjects pertinent to the contract, namely:

1. The measurement of low humidities
2. The occurrence of moisture in the high atmosphere
3. The properties of various surfaces as dependent upon
ambient humidity

This literature survey is currently being brought up to date. The most important periodicals searched were:

1. Chemical Abstracts
2. Meteorological and Geostrophysical Abstracts
3. Science Abstracts

Chemical Abstracts, sometimes overlooked by meteorologists, was by far the most useful source of information in the above subjects. Some of the more outstanding and useful of the seventy-five surveyed papers are referenced (6-9).

REFERENCES

1. Gutnick, Murray, Journal of Geophysical Research 66, 9, 2867, 1962.
2. Murcray, D. G., et al, Journal of Geophysical Research, 65, 11, 3641, 1960.
3. Meteorological and Geostrophysical Abstracts, 12, 8, 1668 (1961).
4. Turville, C. M., Nature, 190, 156 (1961).
5. Danielsen, E. F., Archiv für Meteorologie, Geophysik und Bioklimatologie, Serie A: Band II, 3, 20 (1959).
6. Ebert, Von G., Kolloid Zeitschrift, 161, 2, 129, 1959.
7. Thorp, J. M., Transactions of the Faraday Soc., 55, 3, 442 (1959).
8. Crespi, S., Chemical Abstracts, p. 6034-d, 1949.
9. A. V. Kiseiev, Chemical Abstracts, P. 3459 h, 1958.

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